ESTIMATION OF AIR-FRACTION, SPECIFIC SURFACE AND OTHER PARAMETERS OF MICELLE SYSTEMS—WOOL—LOW ANGLE X-RAY METHODS

T. RATHO AND B. C. PANDA

REGIONAL ENGINEERING COLLEGE, ROURKELA

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ABSTRACT. This paper deals with the estimation of the percentage of air, the specific surface, the length of coherence, the range of inhomogeneity and the characteristic number of a sample of wool, Scottish Blackface, from England. The low angle scattering camera after Kratky (1958) was used for the experimental measurements. The calculations are similar to those applied by Porod (1951) to two phase systems.

INTRODUCTION

The analysis of the diffraction pattern obtained under small angle scattering is due to Guinier (1937, 1939 and 1943). He introduced the idea of "Particle scattering," continuous low angle scattering considered to be a non-coherent scattering of the individual particles. It can be easily seen that this theory will apply only to dilute systems. During the same period, however, Kratky and his co-workers made an attempt to explain the scattering effects of densely packed colloidal systems on the basis of interparticular interference. This led to a good treatment of some of the micelle systems by Kratky (1938, 1942 and 1949) and also by Porod (1949 and 1951). A large volume of work has also appeared in recent years (Kratky 1962 Porod 1961). We have in this paper followed the considerations of Kratky to find out the parameters of the sample of wool belonging to the densely packed systems.

For a thorough analysis of low angle scattering the following assumptions have also been made.

(i) The incoherent Compton scattering is neglected as we are here concerned with very low angles of the order of 10^{-3} of a radian. Further as this is a densely packed system, the coherent scattering effects are very high compared to the very low effects due to Compton scattering.

(ii) The Babinet's reciprocal relation in Optics is assumed to be valid.

Low angle treatments of the micelle systems allow only the estimation of such parameters common to both the phases and also of the statistical mean values of certain lengths known as the range of inhomogeneity "l_r" and the distance of heterogeneity or the extent of coherence l_c according to Porod (1961). We have

here tried to find out these above quantities from our experimental observations on this particular sample of wool. It is also very interesting to find out the percentage of air fraction in it, while this may throw light on the textile properties of the substance.

EXPERIMENTAL

The source of x-rays was a Philips unit fitted with a copper target. The low angle scattering camera of Kratky (1958) fitted with photographic arrangement was set up along with a crystal monochromator after Johanson-Guinier (1956) to record the scattered intensities. The sample of wool investigated was of the type Scottish Blackface from England. The density of the compact material is assumed to be 1.35 gm/cc, while the sample had an apparent density of 0.376 gm/cc. The experimental details regarding the purification of the sample and its mode of setting up in the Kratky camera are the same as reported in a paper by us (T. Ratho *et al.* 1965). The process of obtaining the scattered intensity was also the same as in the above paper. It may be mentioned here that for recording a particular angular range of scattering only a single photographic record is necessary, since a monochromator is used. From these measurements therefore it is possible to obtain the scattering angle and the corresponding scattered intensity values. For convenience the angle of scattering 2θ has been represented by x where x is given by

$$x = 2\phi(ap)$$

Here a is the film sample distance and p is the transformation factor of the densitometer curves.

As the sample under investigation has some degree of orientation, it is not necessary to make any slit correction and one can proceed with the smeared-out intensity $\tilde{I}$ values. In order to calculate the integrated primary intensity P_0, the primary beam was recorded on a film twice, once for 15 seconds and again for 25 seconds with a reduction factor of 100/3. After microphotometry of these records the areas of the primary beam cross-sections were found out with the help of a planimeter.

THEORY AND DISCUSSION

(a) *Calculation of* P_0

The two areas of the primary beam cross-sections obtained for times of exposure 15 and 25 seconds were 21.22 cm^2 and 34.95 cm^2 respectively. As the sample was exposed for 6 hours and as the reduction factor of the primary beam is 100/3, we can easily calculate the average value of P_0. It is given by

$$P_0 = \text{Area under the curve} \times \frac{\text{Time of exposure of sample}}{\text{Time of exposure of primary beam}}$$

Therefore, on substituting the above value, we have

$$P_0(15) = \left(\frac{3600\times 6}{15}\right) \quad 21.22 \quad \left(\frac{100}{3}\right) - 1019\times 10^3$$

$$P_0(25) = \left(\frac{3600\times 6}{25}\right) \quad 3495 \quad \left(\frac{100}{3}\right) = 962\times 10^3$$

Therefore the average value of P_0 is 991×10^3.

(b) *The invariant Q*

For calculating the value of the specific surface it is necessary to find out the value of the quantity Q known as the invariant. According to the theories of Debye and Buechе (1949) as well as of Porod (1951), in the case of a two phase system, the invariant Q of a scattering curve is independent of the shape and size of the particles responsible for scattering. On the other hand, it depends on the scattering power of the system. It, however, is not independent of the primary beam intensity. This invariant Q is given by

$$Q = \int_0^\infty I(x)x^2\,dx$$

for a slit corrected intensity ;

or,
$$\tilde{Q} = \int_0^\infty \tilde{I}(x)x\;dx$$

for intensity not corrected for collimation error as in the present case. The value of $\tilde{Q}$ is obtained after drawing $\tilde{I}(x)x$ versus x curve and planimetering the area under it. The value obtained in the present case is 978 cm^2 and is represented as $\tilde{Q}_{exp}$, meaning thereby the experimental value of the invariant.

(c) *Invariant and air-fraction*

The effective sample thickness is given by D

where,
$$D = \frac{d_a}{d_c}\cdot\phi.$$

Here the density of (compact) wool is assumed to be

$$d_c = 1.35$$

and the apparent density is

$$d_a = 0.376$$

where ϕ is the diameter of the Mark capillary container and has a value 1.69 mm.

On substituting the above values we have

$$D = 0.047065 \text{ cm.}$$

The electron density of wool is represented by ρ which is expressed as

$$\rho = d_c \frac{\Sigma O}{\Sigma A} = 1.35(0.535) = 0.7223$$

where, ΣO is the sum of the atomic numbers and ΣA is the sum of the atomic weights.

This $\frac{\Sigma O}{\Sigma A} = 0.535$ is taken here, in the case of wool, to have the same value as proteins.

In order to interpret the invariant $\tilde{Q}_{exp}$ given by $\tilde{Q}_{exp} = \int_0^\infty \tilde{I}(x) \times dx$ whose estimated value is 978 cm^2, we assume that the system contains air.

The theoretical invariant comparable with $\tilde{Q}_{exp}$, is given by

$$\tilde{Q}_{Th} = \frac{7.9 \times 10^{-26}}{2\pi} \cdot \lambda^3 N^2 P_0 D(ap) \rho^2 \omega_1 \omega_2$$

for $\lambda = 1.54$ Å, N being the Avogadros number,

p_0 is the integrated primary intensity,

ω_1 is the volume fraction of air, and

ω_2 is the volume fraction of wool.

On substituting the values of $a = 20.8$, $\rho = 25.4$, $P_0 = 0.991 \times 10^6$, $\rho^2 = 0.5216$ and $D = 0.047$, we get

$$\tilde{Q}_{Th} = 2.1469 \times 10^5 \omega_1 \omega_2.$$

From $\tilde{Q}_{Th.} = \tilde{Q}_{exp.}$ follows,

$$\omega_1 \omega_2 = 4.5572 \times 10^{-3}.$$

That means $\omega_1 \sim 4.5572 \times 10^{-3}$

and $\omega_2 \sim 1$.

Therefore the system contains about 0.5% air.

(d) *Specific surface*

In the case of a two phase system it is at times very convenient to exploit the tail portion of the scattering curve corresponding to high angles of scattering. According to Porod (1951) the tail portion of a smeared-out scattering curve of a general two phase system as in the present case has a decrease proportional to x^{-3}. The tail portion however follows a course x^{-4} for a curve corrected for length collimation error. Homogeneous electron density distribution however is assumed within each phase. The $\tilde{I}(x)x^3$ versus x curve should show therefore an asymptotic behaviour for large values of x in our present case.

We can therefore write

$$\text{Lim } \tilde{I}(x)x^3 = \tilde{k}, \text{ where } \tilde{k} \text{ is a constant.}$$

The relative curve is plotted in Fig. 1 after our experimental observations from Table I, where the value of $\tilde{k}$ is obtained as 380. This value is related to the

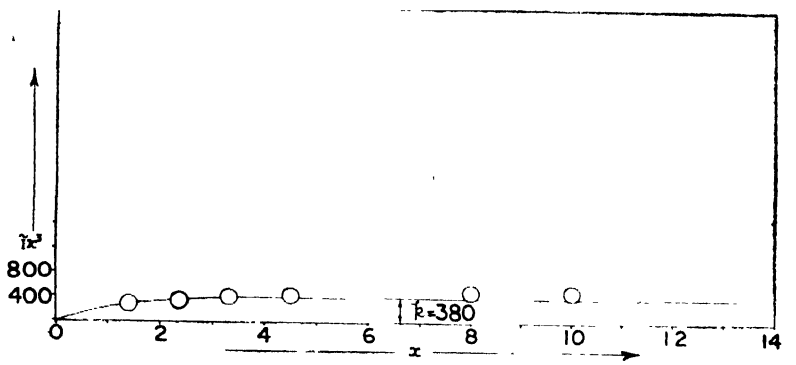

Fig. 1

specific inner surface, i.e. the phase boundary area per unit volume of dispersed phase.

This behaviour of the scattering curve can also be verified by drawing the double logarithmic plot, i.e. log $I(x)$ as a function of log x which should lead to a straight line of slope—3. This is shown in Fig. 2 where a slope of —2.97 is obtained, while the dotted line is the line of slope—3.

The specific surface (per Å^3 sample volume) is given by Porod (1952) as

$$\frac{O}{V} = \frac{8\pi}{\lambda a p} \times \frac{\tilde{k}}{\tilde{Q}_{exp}} \omega_1\omega_2 = \frac{16.32}{a\,p} \times \frac{\tilde{k}}{\tilde{Q}_{exp}} \omega_1\omega_2 \qquad \text{(for } \lambda = 1.54\,\text{Å)}$$

with $\tilde{k} = 380$ and $\omega_1\,\omega_2$ as calculated before we get, on substitution,

$$\frac{O}{V} = \frac{16.32 \times 380 \times 4.5572 \times 10^{-3}}{20.8 \times 25.4 \times 978} = 5.4702 \times 10^{-5}\ \text{cm}^2/\text{Å}^3.$$

The mean dimensions $\bar{l}_1$ and $\bar{l}_2$ of the sample are calculated therefore to be

$$\bar{l}_1 = \frac{4V\omega_1}{O} = 333.28\,\text{Å}$$

and

$$\bar{l}_2 = \frac{4V\omega_2}{O} = 7.3131 \times 10^4\,\text{Å}.$$

In this case $\bar{l}_1$ is practically identical with the reduced length l_r, defined by, according to Porod (1953),

$$\frac{1}{l_r} = \frac{1}{\bar{l}_1} + \frac{1}{\bar{l}_2}$$

and for example $l_r = \frac{4V\omega_1\omega_2}{\Omega}$; since $\omega_2 = 1$

(l_r, the range of inhomogeneity given by the above formula corresponds to that of reduced mass in Mechanics. In interpreting certain results Porod introduces the length l_r known as the "range of inhomogeneity". This is symmetrical with respect to the two average dimensions of the specimen occupied by matter and is built up in the same manner as the reduced mass in Mechanics).

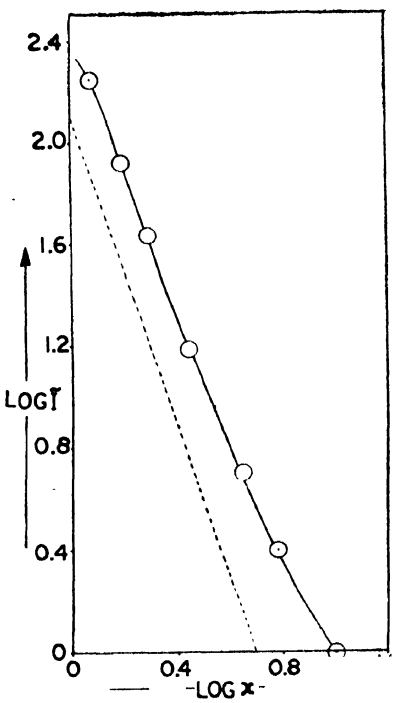

Fig. 2

(e) *Length of coherence* l_c

The integrated scattered energy is given by

$$\tilde{E} = \int_0^\infty \tilde{I}(x)\, dx$$

In order to get the value of $\tilde{E}$ the $\tilde{I}(x)$ versus x curve is drawn and the area under the curve is found out with the help of a planimeter. The value of $\tilde{E}$ obtained

in the present case is 1188.0 cm². The length of coherence l_c is derived from the smeared-out scattering curve according to the relation

$$l_c = \frac{\lambda}{\pi} ap \frac{\int_0^{\infty} \tilde{I}(x)dx}{\int_0^{\infty} \tilde{I}(x)xdx} = 0.490\, ap \frac{\tilde{E}}{\tilde{Q}_{exp}}$$

On substituting the values of E, a and p as $\tilde{E} = 1188.0$, $a = 20.8$ and $p = 25.4$ and $\tilde{Q}_{exp} = 978.0$ we get

$$l_c = 314.48 \text{ Å}.$$

(f) *The characteristic number f*

The characteristic number "f" is given by

$$f = \frac{1}{2} \frac{l_c}{l_r} = \frac{1}{2} \frac{l_c}{l_1} = 0.47181.$$

TABLE I

(Experimental measurements)

x	$\tilde{I}$	$\tilde{I}x^3$	log x	log $\tilde{I}$
1.2	176.0	304.09	0.07918	2.24551
1.30	125.6	275 93	0.11394	2.09895
1.40	105.2	288.66	0.14613	2.02200
1.55	83.6	311.31	0.19033	1.92221
1.70	65.6	322.26	0.23045	1.81690
1.95	43.4	321.81	0.29003	1.63749
2.20	26.9	286.42	0.34242	1.42975
2.35	23.0	298.47	0.37107	1.36173
2.50	18.8	293.76	0.39794	1.27416
2.80	15.2	333.66	0.44716	1.18184
3.05	12.8	363.18	0.48430	1.10721
3.30	11.5	413.24	0.51851	1.66070
3.50	10.0	428.75	0.54407	1.00000
4.00	7.1	454.40	0.60206	0.85126
4.50	5.0	455.62	0.65321	0.69897
5.00	3.9	487.50	0.69897	0.59106
6.00	2.5	540.00	0.77815	0.39794

Although this value is slightly low it is almost the probable value for densely packed systems where the independent micelle are arranged in layers with free space, in between.

CONCLUSION

The specific surface per $Å^3$ sample volume is found to be 5.47×10^{-5} $cm^2/Å^3$. The sample contains about 0.5% of air. The range of inhomogeneity l_r is 333.28 Å. The length of coherence l_c is 314.48 Å. The characteristic number f of the system is 0.472. Further experiments are being undertaken to find out the relation of these quantities with the textile properties of the sample.

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